Partial Translation of JP 10(1998)-208296 A

Publication Date : August 7, 1998
Application No. : 9(1997)-11559
Application Date : January 24, 1997
Applicant : ASAHI CHEM IND CO LTD
[Translation of address omitted]

Title of the Invention : OPTIAL RECORDING MEDIUM

Translation of Column 1, lines 1 - 11

【Claim 1】

A phase transition type information recording medium for use with a short-wavelength laser, comprising, on a substrate, an optical recording layer containing at least Te, wherein an extinction coefficient ka in the amorphous state of the optical recording layer is not more than 2.5 at a wavelength of 400 to 500 nm.

【Claim 2】

The phase transition type information recording medium for use with a short-wavelength laser according to claim 1, wherein the optical recording layer contains hydrogen of not less than 30 ppm and not more than 10000 ppm.

【Claim 3】

An information recording method comprising the step of subjecting the phase transition type information recording medium according to claim 1 or 2 to mark edge recording by using a short-wavelength laser.

Translation of Column 1, line 42 – Column 2, line 45

【0004】

[Problems to be solved by the invention]

A wavelength of a semiconductor laser currently often used in the phase changing type recording method is 680 nm. Therefore, the phase transition recording media that are put in practical application or being developed have optical characteristics suitable for the foregoing wavelength. In this case, normally, a difference between extinction coefficients in the

amorphous state and in the crystalline state is great, thereby causing reflectances in the amorphous state and in the crystalline state to differ significantly from each other. Therefore, an optical contrast necessary for recording can be obtained.

【0005】

However, in the case where a recording medium suitable for a semiconductor laser with a wavelength of 680 nm is used without any change as a recording medium for use with a short-wavelength semiconductor laser with a wavelength of 400 nm to 500 nm, it is impossible to satisfy optical requirements sufficiently. In other words, it is impossible to satisfy optical characteristics while the recording erasure characteristics or stability is ensured at the same time. This is mainly because the difference between the extinction coefficients in the amorphous state and in the crystalline state decreases. Therefore, an effective technology has been desired that can control optical constants (index of refraction, extinction coefficient) of an optical recording layer containing at least Te, which has been put in practical application as an optical recording layer of a phase transition recording medium.

【0006】

The present invention has been made in light of the above-described situations, and an object of the present invention is to provide a phase transition type information recording medium that includes an optical recording layer containing at least Te that has excellent optical characteristics by controlling optical constants of the information recording medium with respect to a wavelength in a range of 400 nm to 500 nm.

【0007】

[Means for solving problems]

As a result of earnest studies for achieving the foregoing object, the inventors of the present invention have discovered that the aforementioned object is achieved by setting the extinction coefficient ka of the optical recording layer in the amorphous state in a specific range. More specifically, the present invention provides the following invention:

(1) A phase transition type information recording medium for use with a short-wavelength laser, comprising, on a substrate, an optical recording layer containing at least Te, wherein an extinction coefficient ka in the amorphous state of the optical recording layer is not more than 2.5 at

a wavelength of 400 to 500 nm;

(2) The phase transition type information recording medium for use with a short-wavelength laser according to the aspect (1), wherein the optical recording layer contains hydrogen of not less than 30 ppm and not more than 10000 ppm;

【0008】

Here, in a preferred embodiment of the present invention, oxygen and/or hydrogen is further contained therein.

(3) An information recording method comprising the step of subjecting the phase transition type information recording medium according to the above aspect (1) or (2) to mark edge recording by using a short-wavelength laser. The following description will explain the present invention in more detail.

【0009】

It is essential that the extinction coefficient ka of the optical recording layer of the present invention in the amorphous state is not more than 2.5 with respect to a wavelength of 400 nm to 500 nm. In the case where the extension coefficient in the amorphous state is more than 2.5, any film configuration cannot obtain excellent optical characteristics and recording/erasing characteristics sufficiently. The extinction coefficient in the amorphous state of not more than 2.5 will suffice, but not less than 0.5 is preferable. In the case where the extinction coefficient in the amorphous state is smaller than 0.5, the absorption decreases, thereby impairing the erasing characteristics.

(19) JAPANESE PATENT OFFICE

PATENT ABSTRACTS OF JAPAN

(11) Publication number: **10208296 A**

(43) Date of publication of application: **07.08.98**

(51) Int. Cl **G11B 7/24**
G11B 7/24
G11B 7/00

(21) Application number: **09011559**

(22) Date of filing: **24.01.97**

(71) Applicant: **ASAHI CHEM IND CO LTD**

(72) Inventor: **OGAWA SHUICHIRO**
TAKEGUCHI KEIGO

(54) **OPTICAL RECORDING MEDIUM**

(57) Abstract:

PROBLEM TO BE SOLVED: To control the optical constant of a specific wavelength region and to obtain a phase transition type information recording medium having excellent optical characteristics by controlling the attenuation constant ka at the amorphous of an optical recording layer contg. at least Te to a specific range.

SOLUTION: This optical recording medium has the optical recording layer contg. at least Te on a substrate. In addition, the attenuation constant ka at the amorphous of the optical recording layer is specified to ≦2.5 at a wavelength of 400 to 500nm. If the attenuation constant at the amorphous is larger than 2.5, optical characteristics and recording and erasing characteristics may not be satisfied even when any film constitution is adopted. The attenuation constant at the amorphous suffices with ≦2.5 but is specified preferably to ≧0.5. If the attenuation constant at the amorphous is smaller than 0.5, absorption decreases and the erasing characteristic is deteriorated. A larger capacity is obtainable by subjecting such recording medium to mark edge recording by using a short-wavelength laser.

(19)日本国特許庁（ＪＰ）　(12) 公開特許公報（Ａ）　(11)特許出願公開番号

特開平10－208296

(43)公開日　平成10年(1998)８月７日

(51)Int.Cl.⁶		識別記号	ＦＩ		
Ｇ１１Ｂ	7/24	５１１	Ｇ１１Ｂ	7/24	５１１
		５２２			５２２Ａ
	7/00			7/00	Ｑ

審査請求　未請求　請求項の数３　ＯＬ　（全５頁）

(21)出願番号　特願平9－11559

(22)出願日　平成９年(1997)１月24日

(71)出願人　000000033
旭化成工業株式会社
大阪府大阪市北区堂島浜１丁目２番６号

(72)発明者　小川　周一郎
静岡県富士市鮫島２番地の１　旭化成工業株式会社内

(72)発明者　竹口　圭吾
静岡県富士市鮫島２番地の１　旭化成工業株式会社内

(54)【発明の名称】　光記録媒体

(57)【要約】
【課題】　波長４００ｎｍ～５００ｎｍレーザに適した光学特性をもつ記録消去特性にすぐれた短波長レーザ用相変化型記録媒体を提供する。
【解決手段】　基板上に少なくともＴｅを含む光記録層を有し、かつ、該光記録層のアモルファスにおける消衰係数kaが波長４００～５００ｎｍにおいて２．５以下となる短波長レーザ用相変化型情報記録媒体を製造する。

1

【特許請求の範囲】

【請求項１】　基板上に少なくともＴｅを含む光記録層を有し、かつ、該光記録層のアモルファスにおける消衰係数kaが波長４００～５００ｎｍにおいて２．５以下であることを特徴とする短波長レーザ用相変化型情報記録媒体。

【請求項２】　光記録層が、３０ｐｐｍ以上１００００ｐｐｍ以下の水素を含有することを特徴とする請求項１記載の短波長レーザ用相変化型情報記録媒体。

【請求項３】　請求項１又は２の相変化型情報記録媒体に短波長レーザを用いてマークエッジ記録を行うことを特徴とする情報記録方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、４００ｎｍ～５００ｎｍ領域の集光したレーザにより、情報の記録、再生、消去が可能な光学式の相変化型情報記録媒体に関するものである

【０００２】

【従来の技術】近年の情報化社会に呼応して、情報の高度化、多量化が進んでおり、高性能大容量の記録媒体の研究開発が活発化している。このような大容量の記録媒体の一つが光ディスクであり、情報の記録、再生が可能な媒体として、ＣＤやＣＤ－ＲＯＭ等が現在大きな市場を形成している。一方、情報の記録、再生、消去が可能な書き換え型光記録材料としては、主として光磁気記録方式と相変化記録方式が知られている。相変化記録方式は、単一ビームでのオーバーライトが可能であり、かつ、それに用いる光学系も単純化できることから、実用化され、さらに、近年、相変化記録方式に用いられる媒体の高密度化の研究開発が急速に活発になってきている。

【０００３】また、近年、短波長半導体レーザの研究が急速に進展しており、４００～４３０ｎｍ付近の波長をもつ半導体レーザが数年後には実用化される勢いである。レーザの波長が半分になることにより、同じ集光レンズを用いてもレーザビームを半分の径に絞ることが可能になり、その結果、面密度としての光ディスクの容量は４倍になる。そのため、４００～４３０ｎｍの波長に対応した優れた光学特性をもつ記録媒体の出現が期待されている。

【０００４】

【発明が解決しようとする課題】現在の相変化型記録方式に多く使用されている半導体レーザの波長は、６８０ｎｍである。従って、現在商品化あるいは開発されている相変化記録媒体はこの波長に適した光学特性を有している。このような場合、通常はアモルファスの消衰係数と結晶の消衰係数の差が大きいので、アモルファスの反射率と結晶の反射率が大きく異なり、記録に必要な光学的コントラストを得ることができる。

2

【０００５】しかしながら、このような６８０ｎｍの波長の半導体レーザに対応した記録媒体を、そのまま４００ｎｍ～５００ｎｍの短波長半導体レーザ用の記録媒体として用いた場合、必要十分な光学特性を満足させることはできない。すなわち、記録消去特性あるいは安定性を確保した上で、光学特性を満足させることができない。これは主にアモルファスの消衰係数と結晶の消衰係数の差が小さくなることに起因している。そのため、相変化記録媒体の光記録層として実用化されている、少なくともＴｅを含む光記録層の光学定数（屈折率、消衰係数）をコントロールすることができる効果的な技術が開発されることが期待されていた。

【０００６】本発明は、上記事情に鑑みて開発されたもので、少なくともＴｅからなる光記録層を有する相変化型記録媒体において、４００～５００ｎｍ波長領域の光学定数をコントロールし、光学特性に優れた相変化型情報記録媒体を提供することを目的とする。

【０００７】

【課題を解決するための手段】本発明者らは、上記目的を達成するために鋭意検討した結果、前記光記録層のアモルファスにおける消衰係数kaを特定の範囲にすることにより、上記目的が達成されることを見いだした。すなわち、本発明は、以下の発明を提供する。

（１）基板上に少なくともＴｅを含む光記録層を有し、かつ、該光記録層のアモルファスにおける消衰係数kaが波長４００～５００ｎｍにおいて２．５以下であることを特徴とする短波長レーザ用相変化型情報記録媒体。

（２）光記録層が、３０ｐｐｍ以上１００００ｐｐｍ以下の水素を含有することを特徴とする上記（１）記載の短波長レーザ用相変化型情報記録媒体。

【０００８】ここで、さらに酸素及び／又は窒素を含有させることは本発明の好ましい態様である。

（３）上記（１）又は（２）の相変化型情報記録媒体に短波長レーザを用いてマークエッジ記録を行うことを特徴とする情報記録方法。以下、本発明を詳細に説明する。

【０００９】本発明の光記録層のアモルファスにおける消衰係数kaは、波長４００～５００ｎｍにおいて２．５以下であることが必須である。このアモルファスの消衰係数が２．５より大きいとどのような膜構成をとっても、よい光学特性および記録消去特性を満足させることができない。このアモルファスの消衰係数は、２．５以下であればよいが、好ましくは０．５以上である。このアモルファスの消衰係数が０．５より小さいと、吸収が小さくなるため、消去特性が劣化する。

【００１０】前記光記録層は、通常は、水素ガスを含む雰囲気中でスパッタすることによって作製できる。また、水素ガス導入管の外側にマイクロ波励起電極を配置して水素ラジカルを発生させて、スパッタ中に光記録層に水素を添加することも可能である。また、タングステ

ンワイヤーを加熱させ、水素ガスを解離させて水素ラジカルを発生させて、スパッタ中、光記録層に水素を添加することも可能である。

【００１１】本発明の光記録層の代表的な作製方法としては、少なくともＴｅからなる合金ターゲットを水素を含む雰囲気下でスパッタする方法を挙げることができる。また、合金ターゲットではなく、それぞれの金属のターゲットを用いて共スパッタしてもよい。あるいは、水素含有の合金ターゲットを用いてスパッタすることもできる。

【００１２】例えば、Ｇｅ、Ｔｅ、Ｓｂからなる合金ターゲット使用した場合は、それぞれの水素化物であるゲルマンガス、スチビンガス、水素化テルルなどを添加ガスとして用いることも可能である。更に酸素ガス、窒素ガスを用いて光記録層に酸素、窒素を水素と併せて含有させることが可能である。また、水素と酸素を光記録層に添加する場合は、スパッタ中の水分を用いることも可能である。水素と窒素を光記録層に添加する場合は、アンモニアなどの窒素水素化合物を使用することも可能である。

【００１３】ここで、水素量が３０ｐｐｍ以下であると、光学特性が十分に確保できないし、水素量が１０００００ｐｐｍより多いと、レーザ光が照射する際膜の劣化が激しく、また、あまりにもアモルファスの消衰係数が小さくなるため消去ができなくなる。好ましい水素量としては、５０ｐｐｍ以上３０００ｐｐｍである。更に、酸素を添加する場合には、酸素と水素の量比が重要である。酸素量が多いと合金の酸化がひどく、記録消去特性が劣化し、使用することができない。

【００１４】本発明で用いる光記録層の膜厚は、光学特性、記録消去特性によって考慮しなくてはならないが、一般的には１０ｎｍ以上５０ｎｍ以下であり、好ましくは、２０ｎｍ以上４０ｎｍ以下である。この膜厚が厚すぎると、記録感度が下がるため好ましくない。この膜厚が薄すぎると、記録消去の繰り返し安定性が極端に悪くなり、かつ、記録コントラストが下がり好ましくない。

【００１５】本発明の光記録媒体で用いる基板としては、ポリカーボネート、アクリル樹脂、エポキシ樹脂、ガラス、アルミニウム、セラミックスなどを用いることができる。　また、光記録層の材料としては、結晶と非晶質との間で可逆的に相変化する少なくともＴｅを含む材料であればよい。少なくともＴｅを含有する光記録層としては、ＧｅＴｅ、Ｇｅ－Ｔｅ－Ｓｂ、Ｉｎ－Ｓｂ－Ｔｅ－Ａｇ、Ｇｅ－Ｓｅ－Ｓｂ、Ｉｎ－Ｓｂ－Ｔｅ、Ｉｎ－Ｓｅ－Ｔｅなどを好ましいものとして挙げることができる。更に好ましくは、Ｇｅ－Ｔｅ－Ｓｂ、Ｉｎ－Ｓｂ－Ｔｅ－Ａｇを挙げることができる。これらの光記録層に添加されるその他の材料としては、さまざまな材料を挙げることができる。このような材料としては、Ａｌ，Ｓｉ，Ｓ，Ａｒ，Ｋ，Ｃａ，Ｔｉ，Ｃｒ，Ｍｎ，Ｆｅ，Ｃｏ，Ｎｉ，Ｃｕ，Ｚｎ，Ｇａ，Ａｓ，Ｓｅ，Ｓｒ，Ｐｄ，Ａｇ，Ｃｄ，Ｉｎ，Ｓｎ，Ｂｒ，Ｂａ，Ｐｔ，，Ａｕ，Ｐｂ，Ｂｉ、Ｃ，Ｎ，Ｏ，Ｆ，Ｂなどを挙げることができる。また、前述の記録層にさまざまな有機物を添加させることもできる。

【００１６】本発明の光記録媒体を構成する、記録層以外の層としては記録層を挟む上層保護層、下層保護層や反射層などを挙げることができる。また、必要ならば更に多層にすることも可能である。保護層の材料としては $ZnS \cdot SiO_2$、Ta_2O_5、SiO_2，ＳｉＯ、Al_2O_3、ＡｌＮ、ZrO_2、TiO_2、ＭｇＯ、GeO_2、Si_3N_4、ＺｎＳ、ＺｎＴｅ、ＢＮなどを用いることができるが、更にＣなどや他にも耐湿性に優れた材料、記録層との密着性に優れた材料やレーザによる記録・消去の際の熱的効果が大きいものを使用することができる。

【００１７】反射層の材料としてはＡｌ、Ａｌ－Ｔｉ、Ａｌ－Ｃｒ、Ａｕ、Ｃｕ、Ｓｉなどを示すことができ、再生信号の増幅効果やレーザ照射によって生ずる熱の拡散効果があるものが好ましい。光記録媒体の作製方法としては、射出成型などで片面にグルーブあるいはピットなどが形成されている基板にスパッタあるいは蒸着などで保護膜下層、光記録層、保護膜上層、反射層などを積層する。ここで用いられる基板の厚みとしては、０．６ｍｍ、１．２ｍｍが最も一般的である。

【００１８】本発明において用いられる短波長レーザとしては、４００～５００ｎｍの発振波長をもつレーザであり、ガスレーザ、半導体レーザ、固体レーザあるいは非線形光学材料を装備したレーザなどを挙げることができる。現状ではＡｒレーザ、非線形光学材料を装備したレーザを使用することができるが、将来的には、４００～５００ｎｍに発光波長をもつ半導体レーザも使用可能である。

【００１９】マークエッジ記録とは、レーザで記録したピットのエッジを情報信号として用いる方法であり、ＣＤ，ＣＤ－ＲＯＭ，ＤＶＤ，ＤＶＤ－ＲＯＭ，ＤＶＤ－Ｒ，ＤＶＤ－ＲＡＭなどの光ディスクの記録方式である。

【００２０】

【発明の実施の形態】以下に本発明の情報記録媒体およびその情報記録媒体の光記録膜の成膜方法について例示する。

（測定解析法）水素量の測定は二次イオン質量分析装置（ＳＩＭＳ：日立製作所製イオンマイクロアナライザー　ＩＭＡ－３）を用いた。但し、二次イオン質量分析装置のみでは絶対量は測定できないので、標準サンプルを不活性ガス融解法（堀場製作所製ＥＭＧＡ－６２１）を用いて一度水素量を測定し、この値を指標にしてＳＩＭＳから水素量を決定した。ここでいう量は質量比である。酸素が存在しているかどうかはやはりＳＩＭＳを用いて測定した。窒素はＸ線光電子分光（ＸＰＳ：VGInst

ruments INC.製ＥＳＣＡＬＡＢ２００－Ｘ）を用いて測定した。また、前述の不活性ガス融解法（堀場製作所製ＥＭＧＡ－６５０）を用いると酸素、窒素の定量も可能である。

【００２１】光学定数の測定法は分光エリプソ装置を用いて測定した。サンプルとしてはシリコンウエハーなどの平滑な基板上に光学定数のわかっている前述の保護膜を積層したのちその後更に光記録膜を積層させたサンプルあるいはまた更にこのサンプル上に保護膜を積層したサンプルを分光エリプソ用測定サンプルとして用いることができる。あるいは、作製した情報記録媒体を適切に不要な層を除去することにより、光記録層の光学定数を測定できるサンプルを作製することも可能である。本発明の光学定数測定にはＪ．Ａ．ＷＯＯＬＬＡＭ ＪＡＰＡＮ製の自動多入射角分光エリプソメータ（ＶＡＳＥ）とそのエリプソメトリーデータ解析ソフトウエア（ＷＶＡＳＥ３２）を用いて測定した。使用入射角は７０゜、７５゜、８０゜の３種類を用いた。通常の波長測定領域は３００ｎｍ以上１７００ｎｍで行ったが、最低４００ｎｍ～５００ｎｍまで測定できれば良い。ここでいう光学定数とは複素屈折率であり、屈折率と消衰係数を示す。

【００２２】

【実施例１】厚さ０．６ｍｍのポリカーボネート基板上にスパッタ法を用いて、下層保護層、光記録層、上層保護層、反射層の順に積層した。下層保護層、上層保護層としてはＺｎＳ＋ＳｉＯ２を用いた。光記録層としてはＳｂ－Ｔｅ－Ｇｅ系合金を用いた。この際、スパッタガスとしてはＡｒガスに１０％の水素ガスを含有する混合ガスを用いた。反射層としてはアルミ合金を用いた。光記録層以外の層を作製する際のスパッタガスはＡｒガスのみを使用した。各層の膜厚はそれぞれ基板側から順に１７０ｎｍ、３００ｎｍ、１２０ｎｍ、１５００ｎｍとした。次にこの上にＵＶ硬化樹脂を５μｍ塗布し、ＵＶで硬化させ、短波長用光ディスクサンプルＡ１を作製した。また、光学定数を測定するサンプルを作製した。シリコンウエハー上にスパッタ法を用いて、光ディスクサンプルＡ１を作製した条件と全く同じ条件で下層保護層、光記録層、上層保護層の順に積層した。それぞれの膜厚は７００ｎｍ、３００ｎｍ、１２０ｎｍであった。このサンプルを分光エリプソを用いて光記録層の光学定数を測定した。保護層の光学定数は予め測定しておきその値を用いて測定、解析を実施した。波長４９０ｎｍにおけるアモルファスサンプルの屈折率、消衰係数はそれぞれ２．６、１．２であった。更に、このサンプルを２７５度、１０分でオーブンを用いて加熱処理をして再度、屈折率、消衰係数を測定した。結晶サンプルの屈折率、消衰係数はそれぞれ、１．５、２．４であった。短波長用光ディスクサンプルＡ１をアルゴンレーザ（波長４８８ｎｍ）を光源とする記録再生装置に装着し、記録再生消去特性の測定を行った。その結果、４８８ｎｍにおける記録パワー及び消去パワーがそれぞれ、８ｍＷ及び４ｍＷでＣＮ比５２ｄＢ、消去率－２６ｄＢを得た。水素ガスの量はＳＩＭＳを用いた測定したところ２６４５ｐｐｍであった。

【００２３】

【比較例１】実施例１と全く同様な方法で光ディスクサンプルＡ２を作製した。但し、今回は光記録層を積層する際のスパッタガスはＡｒガスのみである。この際の記録パワー及び消去パワーは８．５ｍＷ及び４ｍＷで、ＣＮ比４４ｄＢ、消去率－２８ｄＢを得た。また、アモルファスの屈折率、消衰係数はそれぞれ３．０、２．７であり、結晶の屈折率、消衰係数はそれぞれ２．０、３．９であった。水素ガス量はＳＩＭＳを用いて測定したところ２５ｐｐｍであった。

【００２４】

【実施例２】実施例１と同様に短波長用光ディスクサンプルＡ３を作製した。但し、今回は光記録層を作製する際のスパッタガスとしてはＡｒガスに水素ガスと酸素ガスを添加した。作製した膜中の水素量は３４５ｐｐｍであった。酸素量はＳＩＭＳからＡｒガスのみで作製したサンプルに比べ２倍の酸素の存在が確認された。この際の記録パワー及び消去パワーは８ｍＷ及び４．２ｍＷで、ＣＮ比５２ｄＢ、消去率－２７ｄＢを得た。また、アモルファスの屈折率、消衰係数はそれぞれ３．２、１．７であり、結晶の屈折率、消衰係数はそれぞれ１．４、２．０であった。

【００２５】

【実施例３】実施例１と同様に短波長用光ディスクサンプルＡ４を作製した。但し、今回は光記録層を作製する際のスパッタガスとしてはＡｒガスに水素ガスと窒素ガスを添加した。作製した膜中の水素量は１５２３ｐｐｍであった。窒素量はＸ線光電子分光装置の分析で０．４％であった。この際の記録パワー及び消去パワーは７．５ｍＷ及び３．７ｍＷで、ＣＮ比５１ｄＢ、消去率－２７ｄＢを得た。また、アモルファスの屈折率、消衰係数はそれぞれ３．０、１．６であり、結晶の屈折率、消衰係数はそれぞれ１．８、２．４であった。

【００２６】

【比較例２】実施例１と全く同様な方法で光ディスクサンプルＡ５を作製した。但し、今回は光記録層を積層する際のスパッタガスはＡｒガス（６０％）と水素ガス（４０％）である。この際の記録パワーは６．５ｍＷで４４ｄＢであったが消去比は最高で１０ｄＢしかでておらずほとんど消去できていなかった。また、アモルファスの屈折率、消衰係数はそれぞれ２．７、０．４５であり、結晶の屈折率、消衰係数はそれぞれ２．２、１．１であった。水素ガス量はＳＩＭＳを用いて測定したところ１１２２５ｐｐｍであった。

【００２７】

【発明の効果】本発明により、適切な光学定数をもち、記録消去、安定性などのバランスがとれた短波長レーザ用として特に優れた相変化型情報記録媒体が提供され、この短波長レーザ用相変化型情報記録媒体に短波長レーザを用いてマークエッジ記録を行うことにより、大容量化が可能となる。

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **10-208296**

(43)Date of publication of application : **07.08.1998**

(51)Int.Cl. G11B 7/24
G11B 7/24
G11B 7/00

(21)Application number : **09-011559**

(22)Date of filing : **24.01.1997**

(71)Applicant : **ASAHI CHEM IND CO LTD**

(72)Inventor : **OGAWA SHUICHIRO**
TAKEGUCHI KEIGO

(54) OPTICAL RECORDING MEDIUM

(57)Abstract:
PROBLEM TO BE SOLVED: To control the optical constant of a specific wavelength region and to obtain a phase transition type information recording medium having excellent optical characteristics by controlling the attenuation constant ka at the amorphous of an optical recording layer contg. at least Te to a specific range.
SOLUTION: This optical recording medium has the optical recording layer contg. at least Te on a substrate. In addition, the attenuation constant ka at the amorphous of the optical recording layer is specified to ≤2.5 at a wavelength of 400 to 500nm. If the attenuation constant at the amorphous is larger than 2.5, optical characteristics and recording and erasing characteristics may not be satisfied even when any film constitution is adopted. The attenuation constant at the amorphous suffices with ≤2.5 but is specified preferably to ≥0.5. If the attenuation constant at the amorphous is smaller than 0.5, absorption decreases and the erasing characteristic is deteriorated. A larger capacity is obtainable by subjecting such recording medium to mark edge recording by using a short-wavelength laser.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or

application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's
decision of rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

CLAIMS

[Claim(s)]
[Claim 1] The phase change mold information record medium for short wavelength laser with which the extinction coefficient ka which can be set amorphously [have on a substrate the optical recording layer which contains Te at least, and / this optical recording layer] is characterized by being 2.5 or less in the wavelength of 400-500nm.
[Claim 2] The phase change mold information record medium for short wavelength laser according to claim 1 with which an optical recording layer is characterized by containing 30 ppm or more hydrogen 10000 ppm or less.
[Claim 3] The information record approach characterized by using short wavelength laser for claim 1 or the phase change mold information record medium of 2, and performing mark edge record.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the optical phase change mold information record medium in which informational record, playback, and elimination are possible with the laser which 400nm - 500nm field condensed. [0002]
[Description of the Prior Art] In response to an information society in recent years, an informational advancement and many quantification are progressing and researches and developments of the record medium of high performance large capacity are activating. One of such the mass record media is an optical disk, and CD, CD-ROM, etc. form the big commercial scene now as a medium in which informational record and playback are possible. On the other hand, as erasable material for optical recording in which informational record, playback, and elimination are possible, the magneto-optic-recording method and the phase change recording method are mainly known. Over-writing with a single beam is possible for a phase change recording method, and researches and developments of the densification of the medium which is put in practical use and is further used for a phase change recording method from the ability also of the optical system used for it to be simplified in recent years are becoming active quickly.
[0003] Moreover, the semiconductor laser in which research of short wavelength semiconductor laser is progressing quickly, and has the wavelength near 400-430nm is the vigor put in practical use several years after in recent years. When the wavelength of laser becomes half, even if it uses the same condenser lens, it becomes possible to extract a laser beam to a half path, consequently the capacity of the optical disk as surface density increases 4 times. Therefore, the appearance of a record medium with the outstanding optical property corresponding to the wavelength of 400-430nm is expected.
[0004]
[Problem(s) to be Solved by the Invention] The wavelength of the semiconductor laser currently that to a current phase change mold recording method used is 680nm. [many] Therefore, the phase change record medium currently developed [which are developed and is current-commercialized] has the optical property suitable for this wavelength. In such a case, since the difference of an amorphous extinction coefficient and the extinction coefficient of a crystal is usually large, an amorphous reflection factor differs from the reflection factor of a crystal greatly, and optical contrast required for record can be acquired.
[0005] However, when the record medium corresponding to semiconductor laser with a wavelength [such] of 680nm is used as it was as a 400nm - 500nm record medium for short wavelength semiconductor laser, required sufficient optical property cannot be satisfied. That is, an optical property cannot be satisfied after securing a record elimination property or stability. This originates in the difference of an amorphous extinction coefficient and the extinction coefficient of a crystal mainly becoming small. Therefore, it was expected that the effective technique in which the optical constant (a refractive index, extinction coefficient) of the optical recording layer which is put in practical use as an optical recording layer of a phase change record medium and which contains Te at least is controllable

would be developed.
[0006] This invention was developed in view of the above-mentioned situation, controls the optical constant of 400-500nm wavelength field in the phase change mold record medium which has the optical recording layer which consists of Te at least, and aims at offering the phase change mold information record medium excellent in the optical property.
[0007]
[Means for Solving the Problem] this invention persons found out that the above-mentioned purpose was attained by making into the specific range the extinction coefficient ka which can be set amorphously [said optical recording layer], as a result of inquiring wholeheartedly, in order to attain the above-mentioned purpose. That is, this invention offers the following invention.
(1) The phase change mold information record medium for short wavelength laser with which the extinction coefficient ka which can be set amorphously [have on a substrate the optical recording layer which contains Te at least, and / this optical recording layer] is characterized by being 2.5 or less in the wavelength of 400-500nm.
(2) The phase change mold information record medium for short wavelength laser of the above-mentioned (1) publication with which an optical recording layer is characterized by containing 30 ppm or more hydrogen 10000 ppm or less.
[0008] Here, it is the desirable mode of this invention to make oxygen and/or nitrogen contain further.
(3) The information record approach characterized by using short wavelength laser for the above (1) or the phase change mold information record medium of (2), and performing mark edge record. Hereafter, this invention is explained to a detail.
[0009] As for the extinction coefficient ka which can be set amorphously [the optical recording layer of this invention], in the wavelength of 400-500nm, it is indispensable that it is 2.5 or less. If this amorphous extinction coefficient is larger than 2.5, a very good optical property and a record elimination property cannot be satisfied for what kind of film configuration. Although this amorphous extinction coefficient should just be 2.5 or less, it is 0.5 or more preferably. If this amorphous extinction coefficient is smaller than 0.5, since absorption will become small, an elimination property deteriorates.
[0010] Said optical recording layer is producible by usually carrying out a spatter in the ambient atmosphere containing hydrogen gas. Moreover, it is also possible to arrange a microwave excitation electrode on the outside of hydrogen gas installation tubing, to generate a hydrogen radical, and to add hydrogen in an optical recording layer during a spatter. Moreover, a tungsten wire is made to heat, hydrogen gas is made to dissociate, a hydrogen radical is generated, and it is also possible during a spatter to add hydrogen in an optical recording layer.
[0011] The approach of carrying out the spatter of the alloy target which consists of Te at least under the ambient atmosphere containing hydrogen as the typical production approach of the optical recording layer of this invention can be mentioned. Moreover, a ** spatter may be carried out not using an alloy target but using the target of each metal. Or a spatter can also be carried out using the alloy target of hydrogen content.
[0012] For example, when [which consists of germanium, Te, and Sb] alloy target use is carried out, it is also possible to use the germane gas which is each hydride, stibine gas, a hydrogenation tellurium, etc. as addition gas. Furthermore, it is possible to combine oxygen and nitrogen with hydrogen and to make an optical recording layer contain them using oxygen gas and nitrogen gas. Moreover, when adding hydrogen and oxygen in an optical recording layer, it is also possible to use the moisture under spatter. When adding hydrogen and nitrogen in an optical recording layer, it is also possible to use nitrogen hydride, such as ammonia.
[0013] Here, when there are more amounts of hydrogen than 10000 ppm, since an extinction coefficient with it becomes small in case a laser beam irradiates, elimination becomes impossible [an optical property cannot fully secure that the amount of hydrogen is 30 ppm or less, and]. [intense and degradation of the film and] [too much amorphous] As a desirable amount of hydrogen, it is 50 ppm or more 3000 ppm. Furthermore, when adding oxygen, the quantitative ratio of oxygen and hydrogen is important. When there are many amounts of oxygen, oxidation of an alloy is severe, and a record

elimination property can deteriorate and cannot use it.
[0014] Although the thickness of the optical recording layer used by this invention must be taken into consideration with an optical property and a record elimination property, generally it is 10nm or more 50nm or less, and is 20nm or more 40nm or less preferably. If this thickness is too thick, since record sensibility falls, it is not desirable. If this thickness is too thin, the repeat stability of record elimination gets extremely bad, and record contrast falls and is not desirable.
[0015] As a substrate used with the optical recording medium of this invention, a polycarbonate, acrylic resin, an epoxy resin, glass, aluminum, the ceramics, etc. can be used. Moreover, what is necessary is just the ingredient which carries out a phase change reversibly between a crystal and an amorphous substance as an ingredient of an optical recording layer and which contains Te at least. As an optical recording layer which contains Te at least, GeTe, germanium-Te-Sb, In-Sb-Te-Ag, germanium-Se-Sb, In-Sb-Te, In-Se-Te, etc. can be mentioned as a desirable thing. Furthermore, germanium-Te-Sb and In-Sb-Te-Ag can be mentioned preferably. Various ingredients can be mentioned as an ingredient of others which are added by these optical recording layers. As such an ingredient, aluminum, Si, S, Ar, K, calcium, Ti, Cr, Mn, Fe, Co, nickel, Cu, Zn, Ga, As, Se, Sr, Pd, Ag, Cd, In, Sn, Br, Ba, Pt, Au, Pb, Bi, C, N, O, F, B, etc. can be mentioned. Moreover, the above-mentioned record layer can also be made to add various organic substance.
[0016] The upper protective layer and lower layer protective layer whose record layer is pinched as layers other than a record layer, a reflecting layer, etc. which constitute the optical recording medium of this invention can be mentioned. Moreover, if required, it is also possible to make it a multilayer further. Although ZnS-SiO2, Ta 2O5, SiO2, SiO and aluminum 2O3, AlN, ZrO2, TiO2, MgO and GeO2, Si3N4, ZnS, ZnTe, BN, etc. can be used as an ingredient of a protective layer The thermal effectiveness in the case of the record and elimination by the ingredient which was furthermore excellent in moisture resistance also at C etc. and others, the ingredient excellent in adhesion with a record layer, or laser can use a large thing.
[0017] A thing with the spreading effect of the heat which can show aluminum, aluminum-Ti, aluminum-Cr, Au, Cu, Si, etc. as an ingredient of a reflecting layer, and is produced by the magnification effectiveness and laser radiation of a regenerative signal is desirable. As the production approach of an optical recording medium, the laminating of a protective coat lower layer, an optical recording layer, the protective coat upper layer, the reflecting layer, etc. is carried out to the substrate with which the groove or the pit is formed in one side by injection molding etc. by the spatter or vacuum evaporationo. As thickness of the substrate used here, 0.6mm and 1.2mm are the most common.
[0018] As short wavelength laser used in this invention, it is laser with the oscillation wavelength of 400-500nm, and the laser equipped with gas laser, semiconductor laser, solid state laser, or a non-linear optical material etc. can be mentioned. Although Ar laser and the laser equipped with a non-linear optical material can be used in the present condition, the semiconductor laser which has luminescence wavelength in 400-500nm is also usable in the future.
[0019] Mark edge record is an approach using the edge of the pit recorded by laser as an information signal, and is the recording method of optical disks, such as CD, CD-ROM, DVD, DVD-ROM, DVD-R, and DVD-RAM.
[0020]
[Embodiment of the Invention] It illustrates below about the membrane formation approach of the information record medium of this invention, and the optical recording film of the information record medium.
(Measurement analysis method) Measurement of the amount of hydrogen used secondary-ion-mass-spectroscopy equipment (SIMS: Hitachi ion microanalyzer IMA-3). However, since absolute magnitude could not be measured only with secondary-ion-mass-spectroscopy equipment, the amount of hydrogen was once measured for the correlation sample using the inert gas fusion method (Horiba EMGA- 621), this value was made into the index, and the amount of hydrogen was determined from SIMS. An amount here is a mass ratio. Whether oxygen exists or not measured using SIMS too. Nitrogen was measured using X-ray photoelectron spectroscopy (ESCALAB200made from XPS:VGInstruments INC.-X).

Moreover, if the above-mentioned inert gas fusion method (Horiba EMGA- 650) is used, oxygen and the determination of nitrogen are also possible.
[0021] the measuring method of an optical constant -- a spectrum -- it measured using ERIPUSO equipment. the sample to which the laminating of the optical recording film was further carried out after that after carrying out the laminating of the above-mentioned protective coat which the optical constant understands on smooth substrates, such as a silicon wafer, as a sample -- or -- furthermore, the sample which carried out the laminating of the protective coat on this sample -- a spectrum -- it can use as a measurement sample for ERIPUSO. Or it is also possible to produce the sample which can measure the optical constant of an optical recording layer by removing an unnecessary layer for the produced information record medium appropriately. optical constant measurement of this invention -- J.A.WOOLLAM the automatic many angles of incidence made from JAPAN -- a spectrum -- it measured using an ellipsometer (VASE) and its ellipsometry data analysis software (WVASE32). The use incident angle used three kinds, 70 degrees, 75 degrees, and 80 degrees. What is necessary is just to be able to measure to at least 400nm - 500nm, although the usual wavelength measurement field was performed by 300nm or more 1700nm. An optical constant here is complex index of refraction, and a refractive index and an extinction coefficient are shown.
[0022]
[Example 1] The spatter was used on the polycarbonate substrate with a thickness of 0.6mm, and the laminating was carried out to the order of a lower layer protective layer, an optical recording layer, the upper protective layer, and a reflecting layer. ZnS+SiO2 was used as a lower layer protective layer and an upper protective layer. The Sb-Te-germanium system alloy was used as an optical recording layer. Under the present circumstances, as sputtering gas, the mixed gas containing 10% of hydrogen gas was used for Ar gas. The aluminum containing alloy was used as a reflecting layer. The sputtering gas at the time of producing layers other than an optical recording layer used only Ar gas. The thickness of each class could be 170nm, 300nm, 120nm, and 1500nm from the substrate side at order, respectively. Next, applied 5 micrometers of UV hardening resin on this, it was made to harden by UV, and the optical disk sample A1 for short wavelength was produced. Moreover, the sample which measures an optical constant was produced. The spatter was used on the silicon wafer and the laminating was carried out to the order of a lower layer protective layer, an optical recording layer, and the upper protective layer on the completely same conditions as the conditions which produced the optical disk sample A1. Each thickness was 700nm, 300nm, and 120nm. this sample -- a spectrum -- the optical constant of an optical recording layer was measured using ERIPUSO. The optical constant of a protective layer analyzed by measuring beforehand and measuring using the value. The refractive index of the amorphous sample in the wavelength of 490nm and the extinction coefficient were 2.6 and 1.2, respectively. Furthermore, this sample was heat-treated using oven in 275 degrees and 10 minutes, and the refractive index and the extinction coefficient were measured again. The refractive index of a crystal sample and the extinction coefficient were 1.5 and 2.4, respectively. The record regenerative apparatus which makes argon laser (wavelength of 488nm) the light source was equipped with the optical disk sample A1 for short wavelength, and the record playback elimination property was measured. Consequently, the record power and elimination power in 488nm obtained the CN ratio of 52dB, and the rate of elimination of -26dB by 8mW and 4mW, respectively. The amount of hydrogen gas was 2645 ppm when [which used SIMS] measured.
[0023]
[The example 1 of a comparison] The optical disk sample A2 was produced by the completely same approach as an example 1. However, the sputtering gas at the time of carrying out the laminating of the optical recording layer this time is only Ar gas. The record power and elimination power in this case are 8.5mW and 4mW, and obtained the CN ratio of 44dB, and the rate of elimination of -28dB. Moreover, the amorphous refractive index and the extinction coefficient were 3.0 and 2.7, respectively, and the refractive index of a crystal and the extinction coefficient were 2.0 and 3.9, respectively. When hydrogen capacity was measured using SIMS, it was 25 ppm.
[0024]

[Example 2] Optical disk sample A3 for short wavelength was produced like the example 1. However, as sputtering gas at the time of producing an optical recording layer this time, hydrogen gas and oxygen gas were added in Ar gas. The amount of hydrogen in the produced film was 345 ppm. Compared with the sample which produced the amount of oxygen only by Ar gas from SIMS, existence of twice as many oxygen as this was checked. The record power and elimination power in this case are 8mW and 4.2mW, and obtained the CN ratio of 52dB, and the rate of elimination of -27dB. Moreover, the amorphous refractive index and the extinction coefficient were 3.2 and 1.7, respectively, and the refractive index of a crystal and the extinction coefficient were 1.4 and 2.0, respectively.
[0025]
[Example 3] Optical disk sample A4 for short wavelength was produced like the example 1. However, as sputtering gas at the time of producing an optical recording layer this time, hydrogen gas and nitrogen gas were added in Ar gas. The amount of hydrogen in the produced film was 1523 ppm. Nitrogen volume was 0.4% in analysis of X-ray-photoelectron-spectroscopy equipment. The record power and elimination power in this case are 7.5mW and 3.7mW, and obtained the CN ratio of 51dB, and the rate of elimination of -27dB. Moreover, the amorphous refractive index and the extinction coefficient were 3.0 and 1.6, respectively, and the refractive index of a crystal and the extinction coefficient were 1.8 and 2.4, respectively.
[0026]
[The example 2 of a comparison] Optical disk sample A5 was produced by the completely same approach as an example 1. However, the sputtering gas at the time of carrying out the laminating of the optical recording layer this time is Ar gas (60%) and hydrogen gas (40%). Although the record power in this case was 44dB in 6.5mW, only a maximum of 10dB of elimination ratios did not come out, and they were hardly able to be eliminated. Moreover, the amorphous refractive index and the extinction coefficient were 2.7 and 0.45, respectively, and the refractive index of a crystal and the extinction coefficient were 2.2 and 1.1, respectively. When hydrogen capacity was measured using SIMS, it was 11225 ppm.
[0027]
[Effect of the Invention] The phase change mold information record medium which was excellent with this invention especially as an object for short wavelength laser which had a suitable optical constant and was able to balance record elimination, stability, etc. is offered, and large capacity-ization is attained by using short wavelength laser for this phase change mold information record medium for short wavelength laser, and performing mark edge record.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] This invention relates to the optical phase change mold information record medium in which informational record, playback, and elimination are possible with the laser which 400nm - 500nm field condensed.

[Translation done.]

PRIOR ART

[Description of the Prior Art] In response to an information society in recent years, an informational advancement and many quantification are progressing and researches and developments of the record medium of high performance large capacity are activating. One of such the mass record media is an optical disk, and CD, CD-ROM, etc. form the big commercial scene now as a medium in which informational record and playback are possible. On the other hand, as erasable material for optical recording in which informational record, playback, and elimination are possible, the magneto-optic-recording method and the phase change recording method are mainly known. Over-writing with a single beam is possible for a phase change recording method, and researches and developments of the densification of the medium which is put in practical use and is further used for a phase change recording method from the ability also of the optical system used for it to be simplified in recent years are becoming active quickly.
[0003] Moreover, the semiconductor laser in which research of short wavelength semiconductor laser is progressing quickly, and has the wavelength near 400-430nm is the vigor put in practical use several years after in recent years. When the wavelength of laser becomes half, even if it uses the same condenser lens, it becomes possible to extract a laser beam to a half path, consequently the capacity of the optical disk as surface density increases 4 times. Therefore, the appearance of a record medium with the outstanding optical property corresponding to the wavelength of 400-430nm is expected.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] The phase change mold information record medium which was excellent with this invention especially as an object for short wavelength laser which had a suitable optical constant and was able to balance record elimination, stability, etc. is offered, and large capacity-ization is attained by using short wavelength laser for this phase change mold information record medium for short wavelength laser, and performing mark edge record.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The wavelength of the semiconductor laser currently that to a current phase change mold recording method used is 680nm. [many] Therefore, the phase change record medium currently developed [which are developed and is current-commercialized] has the optical property suitable for this wavelength. In such a case, since the difference of an amorphous extinction coefficient and the extinction coefficient of a crystal is usually large, an amorphous reflection factor differs from the reflection factor of a crystal greatly, and optical contrast required for record can be acquired.
[0005] However, when the record medium corresponding to semiconductor laser with a wavelength [such] of 680nm is used as it was as a 400nm - 500nm record medium for short wavelength semiconductor laser, required sufficient optical property cannot be satisfied. That is, an optical property cannot be satisfied after securing a record elimination property or stability. This originates in the difference of an amorphous extinction coefficient and the extinction coefficient of a crystal mainly becoming small. Therefore, it was expected that the effective technique in which the optical constant (a refractive index, extinction coefficient) of the optical recording layer which is put in practical use as an optical recording layer of a phase change record medium and which contains Te at least is controllable would be developed.
[0006] This invention was developed in view of the above-mentioned situation, controls the optical constant of 400-500nm wavelength field in the phase change mold record medium which has the optical recording layer which consists of Te at least, and aims at offering the phase change mold information record medium excellent in the optical property.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] this invention persons found out that the above-mentioned purpose was attained by making into the specific range the extinction coefficient ka which can be set amorphously [said optical recording layer], as a result of inquiring wholeheartedly, in order to attain the above-mentioned purpose. That is, this invention offers the following invention.
(1) The phase change mold information record medium for short wavelength laser with which the extinction coefficient ka which can be set amorphously [have on a substrate the optical recording layer which contains Te at least, and / this optical recording layer] is characterized by being 2.5 or less in the wavelength of 400-500nm.
(2) The phase change mold information record medium for short wavelength laser of the above-mentioned (1) publication with which an optical recording layer is characterized by containing 30 ppm or more hydrogen 10000 ppm or less.
[0008] Here, it is the desirable mode of this invention to make oxygen and/or nitrogen contain further.
(3) The information record approach characterized by using short wavelength laser for the above (1) or the phase change mold information record medium of (2), and performing mark edge record. Hereafter, this invention is explained to a detail.
[0009] As for the extinction coefficient ka which can be set amorphously [the optical recording layer of this invention], in the wavelength of 400-500nm, it is indispensable that it is 2.5 or less. If this amorphous extinction coefficient is larger than 2.5, a very good optical property and a record elimination property cannot be satisfied for what kind of film configuration. Although this amorphous extinction coefficient should just be 2.5 or less, it is 0.5 or more preferably. If this amorphous extinction coefficient is smaller than 0.5, since absorption will become small, an elimination property deteriorates.
[0010] Said optical recording layer is producible by usually carrying out a spatter in the ambient atmosphere containing hydrogen gas. Moreover, it is also possible to arrange a microwave excitation electrode on the outside of hydrogen gas installation tubing, to generate a hydrogen radical, and to add hydrogen in an optical recording layer during a spatter. Moreover, a tungsten wire is made to heat, hydrogen gas is made to dissociate, a hydrogen radical is generated, and it is also possible during a spatter to add hydrogen in an optical recording layer.
[0011] The approach of carrying out the spatter of the alloy target which consists of Te at least under the ambient atmosphere containing hydrogen as the typical production approach of the optical recording layer of this invention can be mentioned. Moreover, a ** spatter may be carried out not using an alloy target but using the target of each metal. Or a spatter can also be carried out using the alloy target of hydrogen content.
[0012] For example, when [which consists of germanium, Te, and Sb] alloy target use is carried out, it is also possible to use the germane gas which is each hydride, stibine gas, a hydrogenation tellurium, etc. as addition gas. Furthermore, it is possible to combine oxygen and nitrogen with hydrogen and to make an optical recording layer contain them using oxygen gas and nitrogen gas. Moreover, when adding hydrogen and oxygen in an optical recording layer, it is also possible to use the moisture under spatter. When adding hydrogen and nitrogen in an optical recording layer, it is also possible to use nitrogen

hydride, such as ammonia.
[0013] Here, when there are more amounts of hydrogen than 10000 ppm, since an extinction coefficient with it becomes small in case a laser beam irradiates, elimination becomes impossible [an optical property cannot fully secure that the amount of hydrogen is 30 ppm or less, and]. [intense and degradation of the film and] [too much amorphous] As a desirable amount of hydrogen, it is 50 ppm or more 3000 ppm. Furthermore, when adding oxygen, the quantitative ratio of oxygen and hydrogen is important. When there are many amounts of oxygen, oxidation of an alloy is severe, and a record elimination property can deteriorate and cannot use it.
[0014] Although the thickness of the optical recording layer used by this invention must be taken into consideration with an optical property and a record elimination property, generally it is 10nm or more 50nm or less, and is 20nm or more 40nm or less preferably. If this thickness is too thick, since record sensibility falls, it is not desirable. If this thickness is too thin, the repeat stability of record elimination gets extremely bad, and record contrast falls and is not desirable.
[0015] As a substrate used with the optical recording medium of this invention, a polycarbonate, acrylic resin, an epoxy resin, glass, aluminum, the ceramics, etc. can be used. Moreover, what is necessary is just the ingredient which carries out a phase change reversibly between a crystal and an amorphous substance as an ingredient of an optical recording layer and which contains Te at least. As an optical recording layer which contains Te at least, GeTe, germanium-Te-Sb, In-Sb-Te-Ag, germanium-Se-Sb, In-Sb-Te, In-Se-Te, etc. can be mentioned as a desirable thing. Furthermore, germanium-Te-Sb and In-Sb-Te-Ag can be mentioned preferably. Various ingredients can be mentioned as an ingredient of others which are added by these optical recording layers. As such an ingredient, aluminum, Si, S, Ar, K, calcium, Ti, Cr, Mn, Fe, Co, nickel, Cu, Zn, Ga, As, Se, Sr, Pd, Ag, Cd, In, Sn, Br, Ba, Pt, Au, Pb, Bi, C, N, O, F, B, etc. can be mentioned. Moreover, the above-mentioned record layer can also be made to add various organic substance.
[0016] The upper protective layer and lower layer protective layer whose record layer is pinched as layers other than a record layer, a reflecting layer, etc. which constitute the optical recording medium of this invention can be mentioned. Moreover, if required, it is also possible to make it a multilayer further. Although ZnS-SiO2, Ta 2O5, SiO2, SiO and aluminum 2O3, AlN, ZrO2, TiO2, MgO and GeO2, Si3N4, ZnS, ZnTe, BN, etc. can be used as an ingredient of a protective layer The thermal effectiveness in the case of the record and elimination by the ingredient which was furthermore excellent in moisture resistance also at C etc. and others, the ingredient excellent in adhesion with a record layer, or laser can use a large thing.
[0017] A thing with the spreading effect of the heat which can show aluminum, aluminum-Ti, aluminum-Cr, Au, Cu, Si, etc. as an ingredient of a reflecting layer, and is produced by the magnification effectiveness and laser radiation of a regenerative signal is desirable. As the production approach of an optical recording medium, the laminating of a protective coat lower layer, an optical recording layer, the protective coat upper layer, the reflecting layer, etc. is carried out to the substrate with which the groove or the pit is formed in one side by injection molding etc. by the spatter or vacuum evaporationo. As thickness of the substrate used here, 0.6mm and 1.2mm are the most common.
[0018] As short wavelength laser used in this invention, it is laser with the oscillation wavelength of 400-500nm, and the laser equipped with gas laser, semiconductor laser, solid state laser, or a non-linear optical material etc. can be mentioned. Although Ar laser and the laser equipped with a non-linear optical material can be used in the present condition, the semiconductor laser which has luminescence wavelength in 400-500nm is also usable in the future.
[0019] Mark edge record is an approach using the edge of the pit recorded by laser as an information signal, and is the recording method of optical disks, such as CD, CD-ROM, DVD, DVD-ROM, DVD-R, and DVD-RAM.
[0020]
[Embodiment of the Invention] It illustrates below about the membrane formation approach of the information record medium of this invention, and the optical recording film of the information record medium.

(Measurement analysis method) Measurement of the amount of hydrogen used secondary-ion-mass-spectroscopy equipment (SIMS: Hitachi ion microanalyzer IMA-3). However, since absolute magnitude could not be measured only with secondary-ion-mass-spectroscopy equipment, the amount of hydrogen was once measured for the correlation sample using the inert gas fusion method (Horiba EMGA- 621), this value was made into the index, and the amount of hydrogen was determined from SIMS. An amount here is a mass ratio. Whether oxygen exists or not measured using SIMS too. Nitrogen was measured using X-ray photoelectron spectroscopy (ESCALAB200made from XPS:VGInstruments INC.-X). Moreover, if the above-mentioned inert gas fusion method (Horiba EMGA- 650) is used, oxygen and the determination of nitrogen are also possible.

[0021] the measuring method of an optical constant -- a spectrum -- it measured using ERIPUSO equipment. the sample to which the laminating of the optical recording film was further carried out after that after carrying out the laminating of the above-mentioned protective coat which the optical constant understands on smooth substrates, such as a silicon wafer, as a sample -- or -- furthermore, the sample which carried out the laminating of the protective coat on this sample -- a spectrum -- it can use as a measurement sample for ERIPUSO. Or it is also possible to produce the sample which can measure the optical constant of an optical recording layer by removing an unnecessary layer for the produced information record medium appropriately. optical constant measurement of this invention -- J.A.WOOLLAM the automatic many angles of incidence made from JAPAN -- a spectrum -- it measured using an ellipsometer (VASE) and its ellipsometry data analysis software (WVASE32). The use incident angle used three kinds, 70 degrees, 75 degrees, and 80 degrees. What is necessary is just to be able to measure to at least 400nm - 500nm, although the usual wavelength measurement field was performed by 300nm or more 1700nm. An optical constant here is complex index of refraction, and a refractive index and an extinction coefficient are shown.

[0022]

[Example 1] The spatter was used on the polycarbonate substrate with a thickness of 0.6mm, and the laminating was carried out to the order of a lower layer protective layer, an optical recording layer, the upper protective layer, and a reflecting layer. ZnS+SiO2 was used as a lower layer protective layer and an upper protective layer. The Sb-Te-germanium system alloy was used as an optical recording layer. Under the present circumstances, as sputtering gas, the mixed gas containing 10% of hydrogen gas was used for Ar gas. The aluminum containing alloy was used as a reflecting layer. The sputtering gas at the time of producing layers other than an optical recording layer used only Ar gas. The thickness of each class could be 170nm, 300nm, 120nm, and 1500nm from the substrate side at order, respectively. Next, applied 5 micrometers of UV hardening resin on this, it was made to harden by UV, and the optical disk sample A1 for short wavelength was produced. Moreover, the sample which measures an optical constant was produced. The spatter was used on the silicon wafer and the laminating was carried out to the order of a lower layer protective layer, an optical recording layer, and the upper protective layer on the completely same conditions as the conditions which produced the optical disk sample A1. Each thickness was 700nm, 300nm, and 120nm. this sample -- a spectrum -- the optical constant of an optical recording layer was measured using ERIPUSO. The optical constant of a protective layer analyzed by measuring beforehand and measuring using the value. The refractive index of the amorphous sample in the wavelength of 490nm and the extinction coefficient were 2.6 and 1.2, respectively. Furthermore, this sample was heat-treated using oven in 275 degrees and 10 minutes, and the refractive index and the extinction coefficient were measured again. The refractive index of a crystal sample and the extinction coefficient were 1.5 and 2.4, respectively. The record regenerative apparatus which makes argon laser (wavelength of 488nm) the light source was equipped with the optical disk sample A1 for short wavelength, and the record playback elimination property was measured. Consequently, the record power and elimination power in 488nm obtained the CN ratio of 52dB, and the rate of elimination of -26dB by 8mW and 4mW, respectively. The amount of hydrogen gas was 2645 ppm when [which used SIMS] measured.

[0023]

[The example 1 of a comparison] The optical disk sample A2 was produced by the completely same

approach as an example 1. However, the sputtering gas at the time of carrying out the laminating of the optical recording layer this time is only Ar gas. The record power and elimination power in this case are 8.5mW and 4mW, and obtained the CN ratio of 44dB, and the rate of elimination of -28dB. Moreover, the amorphous refractive index and the extinction coefficient were 3.0 and 2.7, respectively, and the refractive index of a crystal and the extinction coefficient were 2.0 and 3.9, respectively. When hydrogen capacity was measured using SIMS, it was 25 ppm.

[0024]

[Example 2] Optical disk sample A3 for short wavelength was produced like the example 1. However, as sputtering gas at the time of producing an optical recording layer this time, hydrogen gas and oxygen gas were added in Ar gas. The amount of hydrogen in the produced film was 345 ppm. Compared with the sample which produced the amount of oxygen only by Ar gas from SIMS, existence of twice as many oxygen as this was checked. The record power and elimination power in this case are 8mW and 4.2mW, and obtained the CN ratio of 52dB, and the rate of elimination of -27dB. Moreover, the amorphous refractive index and the extinction coefficient were 3.2 and 1.7, respectively, and the refractive index of a crystal and the extinction coefficient were 1.4 and 2.0, respectively.

[0025]

[Example 3] Optical disk sample A4 for short wavelength was produced like the example 1. However, as sputtering gas at the time of producing an optical recording layer this time, hydrogen gas and nitrogen gas were added in Ar gas. The amount of hydrogen in the produced film was 1523 ppm. Nitrogen volume was 0.4% in analysis of X-ray-photoelectron-spectroscopy equipment. The record power and elimination power in this case are 7.5mW and 3.7mW, and obtained the CN ratio of 51dB, and the rate of elimination of -27dB. Moreover, the amorphous refractive index and the extinction coefficient were 3.0 and 1.6, respectively, and the refractive index of a crystal and the extinction coefficient were 1.8 and 2.4, respectively.

[0026]

[The example 2 of a comparison] Optical disk sample A5 was produced by the completely same approach as an example 1. However, the sputtering gas at the time of carrying out the laminating of the optical recording layer this time is Ar gas (60%) and hydrogen gas (40%). Although the record power in this case was 44dB in 6.5mW, only a maximum of 10dB of elimination ratios did not come out, and they were hardly able to be eliminated. Moreover, the amorphous refractive index and the extinction coefficient were 2.7 and 0.45, respectively, and the refractive index of a crystal and the extinction coefficient were 2.2 and 1.1, respectively. When hydrogen capacity was measured using SIMS, it was 11225 ppm.

[0027]

[Translation done.]